THE ANALYTICAL SEPARATION OF TITANIUM FROM TUNGSTEN, TOGETHER WITH A STUDY OF THE HETEROPOLY-TUNGSTATES.

Thesis submitted for the degree of Ph.D.

of Glasgow University

by

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PREFACE.

That no accurate separation of titanium from tungsten has been devised is commonly admitted by all modern authorities on analytical chemistry.

Of existing methods, that which involves repeated precipitation of the titania with caustic soda or sodium carbonate is recommended by Hillebrand (Hillebrand and Lundell: "Applied Inorganic Analysis" [1929] pp. 455, 551); cf. F. A. Gooch (Proc. Am. Acad. Arts and Sci., New Series, 12 [436] 1884-85); W. F. Hillebrand (U.S. Geol. Surv. Bull., 700, p. 132); V. Auger (Comp. rend., 177 [1923] 1302).

The present research is, primarily, an investigation of the difficulties presented by the separation of titanium from tungsten, and opens with an attempt to achieve a better separation: this attempt was fairly successful.

The experience gained in estimating titanium in presence of tungsten showed quite clearly that these two elements exhibit for one another an affinity which is so remarkable that it suggests formation of a titanium-tungsten compound.

Attempts made to isolate such a compound resulted in the discovery of the tungstotitanic acids.

But this was not all.

During the preparation of 12-tungstotitanic acid, it was discovered that this compound was only one member of an ex-

tensive series of new heteropoly-tungstic acids, and that the synthesis employed to obtain 12-tungstotitanic acid was of general application and could be used extensively in the preparation of other members of the heteropoly-series.

It will be seen, therefore, that the work falls naturally into three parts, of which Part I really constitutes an introduction to Part II:

I. Analytical: The Separation of Titanium from Tungsten.

II. The Tungstotitanic Acids.

III. The Heteropoly-Tungstic Acids in General.

I N D E X.

PART III (contd.).

PART I.

ANALYTICAL.

SEPARATION OF TITANIUM FROM TUNGSTEN.

PART I - ANALYTICAL.

Separation of Titanium from Tungsten.

Introduction.

Jílek and Lukas (Collect. Czechoslov. Chem. Comm., 1 [1929] 263) describe a new method for the estimation of tungsten.

The tungsten is precipitated as quinine arseno-tungstate by addition of quinine hydrochloride to an arseno-tungstate solution containing 1 c.c. of concentrated HCl per 100 c.c. of solution. The precipitate, which comes down in a finely-divided form, must be left for 12 hours to coagulate before it can be filtered.

The precipitate is washed with Solution No. 1, then with Solution No. 2, ignited and weighed as WO_3.

Wash Solution No. 1 contains

2 c.c. conc. HCl
2 c.c. 2% H_3AsO_4 solution
4 c.c. 2% quinine hydrochloride solution
} per 200 c.c.

Wash Solution No. 2 contains

2 c.c. conc. HCl
4 c.c. 2% quinine hydrochloride solution
} per 200 c.c.

Now titanium forms with arsenic acid an arsenate which is insoluble in water, while tungsten, under similar conditions, yields a soluble complex. It will be seen, therefore, that the method of Jílek and Lukas could be used to estimate

the tungsten in the arsenotungstate-containing filtrate after the titanium precipitate had been removed.

That, in brief, is the principle on which the present method for the attempted separation of titanium from tungsten is based.

Experimental.

Following Jílek and Lukas's instructions, a stock solution of sodium tungstate was prepared, and the weight of WO_3 contained in 10 c.c. was found by precipitation as mercurous tungstate.

Results:

I.	Wt. of WO_3	per	10 c.c.	of	Solution	=	·1373 gm.
II.	"	"	"	"	"	=	·1371 gm.
III.	"	"	"	"	"	=	·1374 gm.
IV.	"	"	"	"	"	=	·1371 gm.
Mean	"	"	"	"	"	=	·1372 gm.

The procedure adopted was as follows:

A weighed amount of TiO_2 was fused with Na_2CO_3, the melt extracted with hot water, and 10 c.c. of the sodium tungstate solution run in. H_3AsO_4 added and the solution neutralised. This precipitated the titanium, leaving the tungsten in solution.

One might object to this because extraction of the sodium carbonate melt with water gives almost complete

precipitation of the titanium before the sodium tungstate solution is added; but it was decided to use this method to start with because it was extremely likely that reagents not mentioned in the method of Jílek and Lukas would have to be added, and that, as these reagents might interfere with the precipitation of quinine arsenotungstate, several "blank" estimations were desirable; and the above method would virtually amount to separate "blank" determinations of titanium and tungsten, under conditions similar to those which would be used in the actual separation.

Separation of Titanium from Tungsten.

Method.

A weighed amount (about ·15 gm.) of TiO_2 fused with Na_2CO_3 in a platinum crucible. Melt extracted with hot water, 10 c.c. sodium tungstate solution run in, then 2 c.c. 10% H_3AsO_4 added and the whole well stirred.

HCl added till solution was just acid to methyl orange. Solution was then "buffered" with 1 gm. sodium acetate and boiled. Precipitate filtered and washed with dilute sodium acetate solution.

The precipitate contains titanium.

The filtrate contains tungsten.

Filtrate.

Made just acid with HCl, then 1 c.c. of concentrated HCl per 100 c.c. of solution was added. Heated to boiling

and 20 c.c. of 2% quinine hydrochloride solution run in.

Precipitate of quinine arsenotungstate left to stand for 12 hours, then filtered and washed with Solution No. 1, then with Solution No. 2.

Ignited and weighed as WO_3.

Precipitate.

Filter-paper + precipitate treated with 50 c.c. of concentrated HCl and heated on the sandbath. Precipitate dissolved. Solution diluted and charred paper filtered off and washed with hot water.

Filtrate still contains arsenic.

Hence saturated in the cold with H_2S then heated to boiling.

Boiled to remove excess H_2S.

Precipitate (sulphide of arsenic + sulphur) filtered off and washed with hot water. Filtrate heated to boiling and made slightly alkaline to methyl red with NH_4OH - titanium precipitated as hydroxide.

Precipitate filtered and washed with hot water.

Ignited and weighed as TiO_2.

Results.

Wt. of TiO_2 used.	Wt. of TiO_2 obtained.
·1647 gm.	·1705 gm.

Wt. of WO_3 used.	Wt. of WO_3 obtained.
·1372 gm.	·1352 gm.

Results unsatisfactory; so a titanium "blank" estimation

was carried out.

Method.

As for titanium in the above separation of titanium from tungsten.

Results.

	Wt. of TiO_2 used.	Wt. of TiO_2 obtained.
I	·1590 gm.	·1606 gm.
II	·1770 gm.	·1811 gm.
III	·1597 gm.	·1605 gm.
Mean	·1655 gm.	·1674 gm.

These "blanks" give, for a mean weight of TiO_2 used, a mean positive error of 2 mgm.

Now titanium, when estimated gravimetrically, exhibits a tendency to yield results with a positive error, so the results for the titanium "blank" determinations were not altogether surprising.

But the previous separation of titanium from tungsten gave a positive error, not of 2 mgm., but of 5.8 mgm. for titanium. This abnormally high figure suggests that the sodium tungstate solution might possibly be at fault.

It will have been noticed that the four estimations of the amount of tungstic oxide in 10 c.c. of the stock sodium tungstate solution gave excellent results; but these estimations were carried out immediately after the prepara-

tion of the solution, whereas the estimation of tungsten in the separation of titanium from tungsten was not started till a week later; and it is possible that, in the interval, the sodium tungstate solution had attacked the glass flask in which it was contained. For this reason it was decided to abandon the use of a stock solution of sodium tungstate. In subsequent estimations a weighed amount of tungstic oxide was used, and fused with Na_2CO_3 in a platinum crucible.

Note.

The solution of sodium tungstate was tested 6 months after its preparation, and its behaviour suggested that a large proportion of the tungstate had been converted to tungstosilicate: on acidifying the solution, no immediate precipitate of tungstic acid was formed, and only on leaving the solution to stand for some time did a precipitate appear.

In addition, the glass flask in which the solution had been standing was found to be very markedly etched.

In the descriptions of the various methods that follow, a good deal of repetition is given. This is done deliberately, in the hope that the main outline of the procedure will be clearly understood in spite of the alteration of detail which takes place as each method is succeeded by the next.

Separation of Titanium from Tungsten (TiO_2 + WO_3 being fused with Na_2CO_3 in the same platinum crucible).

Method.

Weighed amounts of TiO_2 and WO_3 respectively fused with Na_2CO_3 in a platinum crucible. Melt extracted with hot water, 2 c.c. 10% H_3AsO_4 solution added and well stirred. HCl added, drop by drop, till solution was just acid to methyl orange, then 1 gm. sodium acetate added and the solution boiled.

Precipitate filtered and washed with dilute sodium acetate solution.

Precipitate contains the titanium.

Filtrate contains the tungsten.

Filtrate.

Made just acid with HCl, then 1 c.c. of concentrated HCl per 100 c.c. of solution was added. Heated to boiling and 20 c.c. of 2% quinine hydrochloride solution run in. The precipitate of quinine arsenotungstate was left to stand for 12 hours, then filtered and washed with Solution No. 1, then with Solution No. 2.

Ignited at a temperature not exceeding 700°C. and weighed as WO_3.

Precipitate (Titanium).

Filter-paper + precipitate treated with 50 c.c. concentrated HCl and heated on sandbath. Precipitate dissolved. Solution diluted and charred paper filtered off and washed

with hot water.

Filtrate still contains arsenic.

Hence solution was saturated in the cold with H_2S, then heated to boiling. Boiled to remove excess H_2S. Precipitate (sulphide of arsenic + sulphur) filtered and washed with hot water. Filtrate heated to boiling, made slightly alkaline to methyl red with NH_4OH and boiled for several minutes.

Precipitate of titanium hydroxide filtered and washed with hot water. Ignited and weighed as TiO_2.

Results.

	Wt.of TiO_2 used.	Wt.of TiO_2 obtained.	Wt.of WO_3 used.	Wt. of WO_3 obtained.
I	·1568 gm.	.1559 gm.	·1334 gm.	·1203 gm.
II	.1554 gm.	·1687 gm.	·1431 gm.	·1320 gm.

The results for titanium are very erratic, but the error for the two tungsten results is approximately the same in each case, viz. slightly more than -10 mgm.

The difficulty attached to this method of fusing the TiO_2 + WO_3 with Na_2CO_3 lies in the fact that, on extraction of the melt with water, the titanium is precipitated in a coarsely-crystalline form, and the large grains of precipitate retain appreciable amounts of sodium tungstate.

For this reason it was decided to try two separate fusions, thus:

Separation of Titanium from Tungsten

(TiO_2 fused with Na_2CO_3 in one crucible.)
(WO_3 fused with Na_2CO_3 in a second crucible).

Method.

A weighed amount of titanic acid was fused with Na_2CO_3 in a platinum crucible. Melt extracted with hot water.

A weighed amount of tungstic acid was fused with Na_2CO_3 in a platinum crucible. Melt extracted with hot water.

The extracts of the two melts were combined, the procedure then being as before (see the previous separation of titanium from tungsten, p. 7).

Results.

	Wt.of TiO_2 used.	Wt.of TiO_2 obtained.	Wt.of WO_3 used.	Wt.of WO_3 obtained.
I	.1532 gm.	·1550 gm.	·1480 gm.	·1496 gm.
II	·1443 gm.	·1492 gm.	·1470 gm.	·1483 gm.

Notes.

1. The titanium precipitates still show a pronounced tendency to give a positive error, which might be due to contamination by arsenic; so one of these precipitates, after being ignited, weighed, and the result found to be too high, was fused with potassium bisulphate in a silica crucible, the melt extracted with water, and the whole subjected to the Gutzeit test for arsenic. No trace of arsenic could be detected, the mercuric chloride paper being still undiscoloured after the test had been in progress for 2 hours.

2. The tungsten results also show a slight positive error. The precipitate of quinine arsenotungstate comes down in a finely-divided, almost colloidal, state at first, and has to be left to stand for 12 hours to coagulate; and, in addition, the precipitate is rather bulky.

These facts suggest that the tungsten error might be due to adsorption of Na^+ ions by the quinine arsenotungstate precipitate.

The only way to overcome this difficulty would be to redissolve the precipitate then reprecipitate it.

Now quinine arsenotungstate presents some analogy to ammonium phosphomolybdate; but there is this difference between the two compounds: ammonium phosphomolybdate can easily be dissolved in NH_4OH, whereas quinine arsenotungstate, when treated with moderately strong NH_4OH, tends to dissolve and then precipitate quinine, which is sparingly soluble in water and hinders the complete solution of the arsenotungstate.

A number of tests were carried out, and finally it was found possible to dissolve quinine arsenotungstate in a hot dilute solution of NH_4OH.

The procedure for the estimation of tungsten was then modified as follows:

Quinine arsenotungstate precipitated from hot acid solution, left to stand for 12 hours, then washed with Solution No. 2 (Solution No. 1 having been found to be unnecessary).

Precipitate treated with 100 c.c. of hot $\frac{N}{20}$ NH_4OH and well stirred. After precipitate had dissolved the solution was re-acidified and quinine arsenotungstate precipitated as before.

Separation of Titanium from Tungsten (Two separate fusions. Tungsten precipitate re-dissolved in NH_4OH).

Method.

As before, with the modification indicated above.

Results.

	Wt. of TiO_2 used.	Wt. of TiO_2 obtained.	Wt. of WO_3 used.	Wt. of WO_3 obtained.
I	·1534 gm.	·1554 gm.	·1360 gm	·1339 gm.
II	·1556 gm.	·1598 gm.	·1387 gm.	·1373 gm.
III	·1417 gm.	·1446 gm.	·1408 gm.	·1407 gm.

For tungsten this method gives results which are reasonably accurate, but the figures for titanium are less satisfactory.

In an attempt to eliminate the titanium error, the procedure was modified as follows, so that the titanium precipitate was redissolved and reprecipitated:-

TiO_2 fused with Na_2CO_3 - melt extracted with hot water.

WO_3 " " - " " "

Extracts of the two melts combined, H_3AsO_4 added and solution made just acid to methyl orange with HCl, "buffered" with sodium acetate and boiled.

Precipitate (I) filtered off and washed with a dilute sodium acetate solution containing a little arsenic acid (1 gm. sodium acetate + ·5 c.c. 10% H_3AsO_4 per 500 c.c.). Filtrate (I) contains most of the tungsten.

Precipitate (I).

Dissolved in 50 c.c. hot concentrated HCl under an air condenser. Solution neutralised with Na_2CO_3, then made just acid to methyl orange with HCl, "buffered" with sodium acetate and boiled. Precipitate (II) filtered and washed with the arsenic acid - sodium acetate solution.

Filtrate (II) added to Filtrate (I), evaporated to 400 c.c. on the sandbath and the tungsten precipitated from HCl solution as quinine arsenotungstate.

Precipitate redissolved in NH_4OH as before, then re-precipitated, ignited and weighed as WO_3.

Precipitate (II) (Titanium).

Dissolved in 50 c.c. hot concentrated HCl, solution cooled and diluted. Arsenic precipitated as the sulphide by saturating in the cold with H_2S, then boiling.

Precipitate filtered and washed with hot water. Filtrate contains the titanium, which is precipitated as hydroxide by addition of NH_4OH.

Results.

	Wt. of TiO_2 used.	Wt. of TiO_2 obtained.	Wt. of WO_3 used.	Wt. of WO_3 obtained.
I	·1412 gm.	·1452 gm.	·1344 gm.	.1370 gm.
II	.1412 gm.	.1441 gm.	.1412 gm.	.1406 gm.
III	.1409 gm.	.1440 gm.	.1160 gm.	.1188 gm.
IV	.1440 gm.	.1496 gm.	.1486 gm.	.1508 gm.
V	.1388 gm.	.1465 gm.	.0951 gm.	.0937 gm.

There is still a persistent and marked positive error for titanium.

Notes.

1. The sodium acetate is a possible source of error. B.D.H.(A.R.) sodium acetate had, up to this point, been used.

Several "blank" estimations of titanium were carried out using (a) B.D.H.(A.R.) sodium acetate.

(b) Merck's (A.R.) sodium acetate.

In each case a positive error was obtained, and as the Merck's reagent, in particular, is above suspicion, it appears that the sodium acetate is not responsible for the error.

2. On p. 9 it was mentioned that the ignited titania precipitate was fused with bisulphate and the aqueous extract subjected to the Gutzeit test: this gave no trace of arsenic.

Ignited titania is, however, extremely difficult to redissolve, so a specimen of TiO_2, weighing approximately ·14 gm., was subjected to the treatment for titanium as in the above separation of tungsten from titanium, and the final precipitate, while still moist, was redissolved in H_2SO_4.

With this solution the Gutzeit test gave a pronounced arsenic stain. Hence the positive error for titanium appears to be due to arsenic.

Titanium can be separated from arsenic acid by precipitation with cupferron from an acid solution containing tartaric acid - W. M. Thornton (Am. J. Sci., 37, [1914] 407).

This method was used as follows:

Titanium: "blank" estimation.

TiO_2 fused with Na_2CO_3. Melt extracted with hot water. 2 c.c. 10% H_3AsO_4 solution added, the solution made just acid to methyl orange with HCl, "buffered" with sodium acetate and boiled.

Precipitate filtered and washed with the H_3AsO_4-NaĀ solution (1 gm. sodium acetate + ·5 c.c. 10% H_3AsO_4 per 500 c.c.).

Precipitate redissolved in a mixture of 1 c.c. 10% H_3AsO_4 + 40 c.c. concentrated HCl by heating on the sandbath. Solution cooled, 10 c.c. 10% H_3AsO_4 added and solution made just alkaline to methyl orange with Na_2CO_3, then just acid

with HCl, "buffered" with sodium acetate and boiled, filtered and washed as before.

Precipitate + filter-paper-pulp dissolved in a mixture of { 20 c.c. concentrated H_2SO_4 / 10 c.c. concentrated HNO_3 } and heated on the sandbath till no more brown fumes were evolved. Solution cooled and a further 10 c.c. concentrated HNO_3 added, then heated as before.

This removed the filter-paper.

Solution taken to SO_3 fumes. Cooled, then cover-glass and inside of beaker washed with water. Evaporated again to SO_3 fumes to remove nitric acid. Solution cooled, diluted to 100 c.c., 20 c.c. 10% tartaric acid solution added and diluted to 200 c.c.*

25 c.c. 6% cupferron run in with brisk stirring. Precipitate left to stand for several minutes. Filtered and washed with a solution containing

{ 10 c.c. concentrated H_2SO_4 / 10 c.c. 6% cupferron } per 300 c.c.

Precipitate ignited and weighed as TiO_2

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* It is better not to dilute the solution too much until the tartaric acid has been added, otherwise titanium arsenate may be precipitated.

Results.

	Wt. of TiO_2 used.	Wt. of TiO_2 obtained.
I	.1411 gm.	.1426 gm.
II	.1452 gm.	.1460 gm.

These results for Ti are satisfactory, so this method was used in the separation.

Separation of Titanium from Tungsten.

TiO_2 + WO_3 fused with Na_2CO_3. Melt extracted with boiling water, 5 c.c. 10% H_3AsO_4 added, solution made just acid to methyl orange with HCl, "buffered" with sodium acetate, boiled, filtered and washed with the H_3AsO_4-NaA solution.

Filtrate (major part of the tungsten) - evaporated to 150 c.c. on sandbath.

Precipitate (Titanium + residual tungsten) - dissolved in a mixture of 1 c.c. 10% H_3AsO_4 } by heating on the sandbath.
40 c.c. conc. HCl }

Solution cooled, 10 c.c. 10% H_3AsO_4 added, diluted to 200 c.c., made just alkaline to methyl orange with Na_2CO_3, then just acid with HCl, "buffered" with 1 gm. sodium acetate, boiled, filtered and washed as before, filtrate (residual tungsten) being added to the first filtrate containing most of the tungsten and the whole evaporated to 400 c.c.

Tungsten.

Solution (400 c.c.) made acid with HCl and quinine arsenotungstate precipitated, washed, redissolved in NH_4OH and reprecipitated as previously described.

Ignited and weighed as WO_3.

Titanium.

Precipitate dissolved in a mixture of

20 c.c. concentrated H_2SO_4 } then treated as described for
10 c.c. concentrated HNO_3

the titanium "blank" estimation (p.15).

Cupferron precipitate ignited in a platinum crucible and weighed as TiO_2.

Results.

Wt.of TiO_2 used.	Wt.of TiO_2 obtained.	Wt. of WO_3 used.	Wt. of WO_3 obtained.
.1378 gm.	.1474 gm.	.1520 gm.	.1420 gm.

Notes.

1. When the titanium precipitate was found to be practically 10 mgm. too heavy, it was fused with Na_2CO_3 and the melt extracted with boiling water.

5 c.c. 10% H_3AsO_4 added, solution made just acid to methyl orange with HCl, "buffered" with sodium acetate and boiled. Precipitate (titania) filtered off.

Filtrate acidified with HCl and quinine hydrochloride added.

Precipitate formed; therefore tungsten present. Thus the titania precipitate contained some tungsten.

2. It will have been observed that the titania and the tungstic acid were fused with sodium carbonate in the same crucible, with the result that, when the melt was extracted with water, the coarsely-crystalline titanium residue would

certainly retain some tungsten. Thus some tungsten is present in the final titania precipitate.

There seemed to be two possible ways of overcoming this difficulty:

(A) A treatment of the sodium carbonate melt which would dissolve the titanium as well as the tungsten.

(B) Repetition of the Na_2CO_3 fusion and extraction with water, in order to decrease the amount of tungsten bound up in the insoluble titanium residue.

Case (A).

Treatment of the Na_2CO_3 melt with an acid - H_2O_2 solution in the hope of dissolving the titanium residue.

Method.

TiO_2 + WO_3 fused with Na_2CO_3.

Melt extracted with a solution containing

10 c.c. concentrated H_2SO_4
30 c.c. H_2O_2 solution (10 vols.) } per 150 c.c.

After effervescence had become less vigorous, the extract was heated on the waterbath. Some residue remained undissolved.

10 c.c. 10% H_3AsO_4 + 6 c.c. perhydrol added and again heated; but some residue still remained.

The extraction of the Na_2CO_3 melt with H_2O_2 + H_2SO_4 was repeated under varying conditions, but it was never found possible to get the titanium completely into solution.

In some cases the major part of the titanium residue dissolved, then a yellow precipitate* containing both titanium and tungsten was thrown down.

From the point of view of getting the titanium permanently into solution, this method was a failure. It was therefore decided that method (B) would have to be adopted.

(* This yellow precipitate was probably a solid tungstotitanic or pertungstotitanic acid. Cf. 10-tungstotitanic acid, p. 52).

Case (B).

Repetition of the Na_2CO_3 fusion and extraction with water.

Method.

1st fusion.

TiO_2 + WO_3 fused with Na_2CO_3. Melt extracted with 200 c.c. boiling water. 5 c.c. 10% H_3AsO_4 added and solution made just acid to methyl orange with HCl. 10 c.c. 10% sodium acetate solution added and boiled.

Precipitate filtered and washed with a solution containing 1 c.c. 10% sodium acetate per 100 c.c. Precipitate ignited in a platinum crucible at a temperature not exceeding 700°C.

Residue subjected to 2nd fusion.

Filtrate contains the major part of the tungsten.

2nd fusion.

Residue fused with Na_2CO_3. Melt extracted with 200 c.c. boiling water. 5 c.c. 10% H_3AsO_4 added, solution

made just acid to methyl orange with HCl, 10 c.c. 10% sodium acetate solution added and boiled.

Precipitate filtered and washed with a solution containing 1 c.c. of 10% sodium acetate per 100 c.c. Filtrate added to first tungsten filtrate. Precipitate dissolved in a mixture of $\left.\begin{matrix}20 \text{ c.c. concentrated } H_2SO_4 \\ 10 \text{ c.c. concentrated } HNO_3\end{matrix}\right\}$ and taken to SO_3 fumes. Coverglass and sides of beaker washed with water and again taken to SO_3 fumes.

Solution cooled, diluted to 100 c.c., 20 c.c. 10% tartaric acid added, then diluted to 200 c.c.

Cooled in ice, 25 c.c. 6% cupferron added, left to stand for several minutes, then filtered and washed with a solution containing $\left.\begin{matrix}10 \text{ c.c. concentrated } H_2SO_4 \\ 10 \text{ c.c. } 6\% \text{ cupferron}\end{matrix}\right\}$ per 300 c.c.

Ignited in a platinum crucible and weighed.

Tungsten.

Combined tungsten filtrates evaporated to 400 c.c. Heated to boiling and solution made just acid to methyl orange with HCl. 20 c.c. 2% quinine hydrochloride added, then 4 c.c. concentrated HCl. Precipitate left to stand for 12 hours.

Filtered and washed with Solution No. 2.

Precipitate redissolved in 100 c.c. hot $\frac{N}{20}$ NH_4OH. Solution made just acid to methyl red with HCl.

Then added: $\left.\begin{matrix}1.3 \text{ c.c. concentrated HCl} \\ 2 \text{ c.c. } 10\% \ H_3AsO_4 \\ 20 \text{ c.c. } 2\% \text{ quinine hydrochloride}\end{matrix}\right\}$

Precipitate of quinine arsenotungstate well stirred and left to stand for 12 hours.

Filtered, washed with solution No. 2, ignited and weighed as WO_3.

Results.

	Wt.of TiO_2 used.	Wt.of TiO_2 obtained.	Wt.of WO_3 used.	Wt. of WO_3 obtained.
I	.1460 gm.	.1457 gm.	.1392 gm.	.1398 gm.
II	.1414 gm.	.1446 gm.	.1492 gm.	.1456 gm.
III	.1294 gm.	.1309 gm.	.1304 gm.	.1280 gm.

These results were obtained by the method involving two sodium carbonate fusions.

The method was extended to three fusions, thus:

Separation of Titanium from Tungsten.

1st fusion.

TiO_2 + WO_3 fused with Na_2CO_3. Melt treated with 200 c.c. boiling water. 5 c.c. 10% H_3AsO_4 added and solution made just acid to methyl orange with HCl, 10 c.c. 10% sodium acetate added and boiled.

Precipitate filtered and washed with a solution containing 1 c.c. 10% sodium acetate per 100 c.c.

Precipitate + filter-paper returned to platinum crucible and ignited at a temperature not exceeding 700°C.

Filtrate contains the major part of the tungsten.

2nd fusion.

Residue fused with Na_2CO_3. Melt treated with 200 c.c. boiling water. 5 c.c. 10% H_3AsO_4 added and solution made just acid to methyl orange with HCl. 10 c.c. 10% sodium acetate added and boiled.

Precipitate filtered and washed with a solution containing 1 c.c. 10% sodium acetate per 100 c.c. Filtrate added to first tungsten filtrate.

Precipitate + filter-paper returned to platinum crucible and ignited at a temperature not exceeding 700°C.

3rd fusion.

Residue fused with Na_2CO_3. Melt treated with 200 c.c. boiling water. 5 c.c. 10% H_3AsO_4 added and solution made just acid to methyl orange with HCl. 10 c.c. 10% sodium acetate added and boiled.

Precipitate filtered and washed with a solution containing 1 c.c. 10% sodium acetate per 100 c.c. Filtrate added to first and second tungsten filtrates.

Titanium.

Precipitate + filter-paper treated with a mixture of

20 c.c. concentrated H_2SO_4
10 c.c. concentrated HNO_3
} and taken to SO_3 fumes.

Coverglass and sides of beaker washed with water and again taken to SO_3 fumes.

Cooled, diluted to 100 c.c., 20 c.c. 10% tartaric acid

added and diluted to 200 c.c. Cooled in ice, 25 c.c. 6% cupferron added and precipitate left to stand for several minutes. Filtered and washed with a solution containing

10 c.c. concentrated H_2SO_4
10 c.c. 6% cupferron
} per 300 c.c.

Ignited in a platinum crucible and weighed.

Tungsten.

Combined tungsten filtrates evaporated to 400 c.c. Solution heated to boiling, made just acid to methyl orange with HCl, then 20 c.c. 2% quinine hydrochloride + 4 c.c. concentrated HCl added.

Precipitate well stirred and left to stand for 12 hours. Filtered and washed with Solution No. 2.

Precipitate redissolved in 100 c.c. hot $\frac{N}{20}$ NH_4OH. Solution made just acid to methyl red with HCl, then added

1.3 c.c. concentrated HCl
2 c.c. 10% H_2AsO_4
20 c.c. 2% quinine hydrochloride
}

Precipitate well stirred and left to stand for 12 hours. Filtered and washed with Solution No. 2.

Ignited and weighed as WO_3.

Results.

	Wt. of TiO_2 used.	Wt. of TiO_2 obtained.	Wt. of WO_3 used.	Wt. of WO_3 obtained.
I	.1399 gm.	.1414 gm.	.1404 gm.	.1416 gm.
II	.1415 gm.	.1413 gm.	.1386 gm.	.1384 gm.

Notes.

1. The titanium precipitate weighing .1414 gm. was fused with Na_2CO_3, extracted with water, 5 c.c. 10% H_3AsO_4 added, made just acid to methyl orange with HCl, "buffered" with sodium acetate and boiled.

Precipitate (titanium) filtered off.

Filtrate acidified with HCl and quinine hydrochloride added. No immediate precipitate - on being left to stand for three days only an extremely small precipitate of quinine arsenotungstate was obtained.

Therefore titanium precipitate is virtually free from tungsten.

2. The tungsten precipitate weighing .1416 gm. was fused with Na_2CO_3. Melt extracted with boiling water gave no precipitate.

To the extract of the melt added 1 c.c. of syrupy phosphoric acid, then 1 c.c. concentrated H_2SO_4 + 1 c.c. perhydrol, the whole being diluted to 100 c.c. in a graduated flask.

This solution was compared in the colorimeter with a solution containing 1 mgm. Ti + 1 c.c. syrupy phosphoric acid + 1 c.c. concentrated H_2SO_4 + .2 gm. $Na_2WO_4.2H_2O$ (this being the amount of sodium tungstate which contained ·14 gm. of WO_3) per 100 c.c. Comparison was very difficult as the solution to be tested was of too weak a colour; but the test

showed that the tungsten precipitate could not have contained more than .3 mgm. of titanium.

Summary.

The preceding method appears to be capable of giving a reasonably accurate separation of titanium from tungsten; it is however rather tedious, owing to the necessity for repeated fusions and precipitations.

From the start it had been apparent that the separation was one of extraordinary difficulty; and the extreme ease with which titanium lost its individuality in presence of tungsten, suggested formation of a titanium-tungsten compound.

The evidence in favour of the existence of such a compound was too great to be disregarded; so attempts were made to isolate it. As a result, the tungstotitanic acids were discovered; and it is with these that we must now deal.

PART II.

THE TUNGSTOTITANIC ACIDS.

A. INTRODUCTION.

cf. Gmelin's Handbuch der anorganischen Chemie 8. Auflage. System Nummer 54. Wolfram, p. 383

The Tungstotitanic Acids.

Historical.

According to R. Lecarme and D. Klein (Bl. Soc. Chim. [2] 36 [1881] 17) two series of tungstotitanates should exist:-

I. Derivatives of 12-tungstotitanic acid, $4H_2O.TiO_2.12WO_3x\ H_2O$.

II. Derivatives of 10-tungstotitanic acid, $4H_2O.TiO_2.10WO_3x\ H_2O$.

To isolate the free acids, the corresponding mercury salts were treated with HCl and H_2S to precipitate the mercury, and the moderately-concentrated solutions were evaporated in vacuo.

The existence of these compounds could not be confirmed by L. A. Hallopeau (Ann. Chim. Phys. [7] 19 [1900] 123) and remains, therefore, up to the present, in doubt.

Since it seems quite reasonable to assume that the tungstotitanates will, in many respects, be analogous to the tungstosilicates, a study of the latter compounds becomes necessary.

The Tungstosilicic Acids.

Historical.

The first data concerning the tungstosilicates come from C. Marignac (Compt. rend. 55 [1862] 888; Lieb. Ann. 125 [1862] 366; Ann. Chim. Phys. [3] 69 [1863] 5, 12, 81) who discovered compounds containing silicic acid in the mother-liquors of ammonium tungstate, and who isolated the first tungstosilicates.

L. 338-340

Very probably, the compounds already described by A.

Laurent (Ann. Chim. Phys. [3] 21 [1847] 54) as polytungstates, and the ammonium metatungstate prepared by A. Riche (Ann. Chim. Phys. [3] 50 [1857] 62) contained tungstosilicate.

The classical researches of C. Marignac (Ann. Chim. Phys. [4] 3 [1864] 5) led to a clear distinction of 3 tungstosilicic acids: by heating a solution of potassium or ammonium paratungstate with gelatinous silicic acid, a complex acid is formed, which contains 12.WO_3 to 1.SiO_2 and was called "silicotungstic acid."

This furnishes the most important acid of the group, an acid which is very stable and exists in two well-crystallised hydrates.

A second 12-tungstic acid was, to distinguish it from the first, described as "tungstosilicic acid."

For both acids, series of salts are known, which are, however, essentially different from one another.

The third acid prepared by C. Marignac (loc. cit.) contained 10.WO_3 to 1.SiO_2 and was known as "silicodecatungstic acid." This nomenclature, though customary for a long time, was later replaced by the clearer system of A. Rosenheim and J. Jaenicke (Z. anorg. Ch. 101 [1917] 240):

$H_8[Si(W_2O_7)_6]28(22)H_2O$	$H_8[Si(W_2O_7)_6]20.H_2O$	$H_8[SiO(W_2O_7)_5]3H_2O$
12-tungstosilicic acid.	Iso-12-tungstosilicic acid.	10-tungstosilicic acid.

Constitution.

According to the hypotheses of A. Miolati (J. pr. Ch. [2]

77 [1908] 439, 446) and A. Rosenheim and J. Pinsker (Z. anorg. Ch. 70 [1911] 73), A. Rosenheim, J. Pinsker, R. Haeberle and R. Bilecki (Z. Elektroch. 17 [1911] 694, 696), the tungstosilicic acids are derived from a silicic acid $H_8[SiO_6]$ in which 6(12-tungstosilicic acid) or 5 oxygen atoms (10 tungstosilicic acid) are replaced by W_2O_7 groups.

According to this theory of constitution the phenomena of isomerism are not made clear. But omission of the assumption of W_2O_7 groups and interpretation of the limiting type $H_8[SiO_6]$ as the hydrate $Si\begin{matrix}(H_2O)_2\\(OH)_4\end{matrix}$ of silicic acid, $Si(OH)_4$, yields, on inclusion of $12.WO_3$-groups, the constitutional formula

$$H_8\left[Si\begin{matrix}O_2\\O_4\end{matrix}''(WO_3)_{12}\right]$$

with mono- and di- valent oxygen.

Sterically, this formula lends itself to a cubic-octahedral arrangement of the atoms or groups of atoms.

The phenomena of isomerism can, according to this configuration, be explained as cis-trans isomerism - P. Pfeiffer (Z. anorg. Ch. 105 [1919] 26, 31).

With regard to at least 18 molecules of the water of crystallisation, the complex can so be built up that 12 octahedra, with W as central atom, lie shell-wise round the central SiO_4-tetrahedron; each octahedron is always linked through an oxygen atom with three neighbouring octahedra, and the free octahedron-angles (altogether 12 x 3 = 36) are attached to -OH groups.

This structure corresponds to the formula

$$H_4\left[SiO_4\ W_{12}\ O_{18}\ (OH)_{36}\right]$$

The strongly-distorted octahedra have 9 short sides of about 2.65 Å, and 3 longer sides of about 3.02 Å in length; in the SiO_4-group the following dimensions apply:

O - O = about 2.60 Å.

Si - O = about 1.59 Å.

Since the shell surrounding the SiO_4-kernel is electrically neutral, the complex anion has the charge of the SiO_4-group itself.

The structure of the less-heavily hydrated acids was also made clear in this way, for 2 octahedra of neighbouring complexes touch at one or more angles, with elimination of water.

Similarly the constitution of the iso-acid was elucidated, - possible dimensions: D_{3d} or D_{3h} - L. Pauling (J. Am. Soc. 51 [1929] 2871, 2877).

Similar structures are given by A. G. Scroggie and G. L. Clark (Pr. nat. Acad. Washington, 15 [1929] 6) whereby the O-atoms of the central SiO_4-group are linked with four thereby-distinguished W atoms, which are also the carriers of the four acid OH-groups.

By formation of an 8-basic salt (see "Basicity") still further OH-groups are ionised and neutralised. E. O. North and G. D. Beal (J. Am. pharm. Assoc., 13 [1924] 892) have also derived schematic structural formulae from orthosilicic acid

$Si(OH)_4$.

Similar structures (bimolecular) for the iso-acid and for unsaturated acids, on the grounds of their inner constitution, are given by A. Bruckl and B. Hahn (Monatsch. 59 [1932] 201).

A. Rosenheim and J. Jaenicke (Z. anorg. Ch. 100 [1917] 325) have also worked extensively on theories of constitution.

Basicity.

The question of the basicity of the tungstosilicic acids is very much debated in the literature.

All three acids were regarded as 8-basic by C. Marignac (Ann. Chim. Phys. [4] 3 [1864] 7). The normal 12-tungstosilicic acid, which, principally, was investigated in this judgment, forms, according to Marignac (loc. cit.) 4-basic (acid) and 8-basic (neutral) salts.

G. Wyrouboff (Bl. Soc. Min. 19 [1896] 228) described the same salt-types as neutral and basic salts.

The best-defined are the so-called 4-basic salts. The evidence supplied by conductivity, on neutralisation of the free acid with alkali, indicates the existence of only 4-basic salts; similarly, the conductivity of the free acid corresponds to a 4-basic acid. Cf. H. Copaux (Z. anorg. Ch. 74 [1912] 355, 360; Ann. Chim. Phys. [8] 26 [1912] 29, 36; Compt. rend. 156 [1913] 72, 73; Bl. Soc. Chim. [4] 13 [1913] 326, 329) and the neutralisation curves of L. Malaprade (Ann. Chim. [10] 11 [1929] 184).

Experiments on the dehydration of the free acid show that

only 2 molecules of water are firmly bound, and that, on loss of these two molecules of water of constitution, a change of crystal structure takes place - A. G. Scroggie and G. L. Clark (Pr. nat. Acad. Washington, 15 [1929] 5).

As further proof of the 4-basicity, the alkaloid compounds were brought forward: these contained a maximum of 4 molecules of alkaloid to 1 molecule of acid - E. O. North and G. D. Beal (J. Am. pharm. Assoc. 13 [1924] 895); L. Lematte, G. Boinot, E. Kahane and M. Kahane (Compt. rend. 191 [1930] 1130); E. Kahane and M. Kahane (Bl. Soc. Chim. [4] 49 [1931] 559).

Of the 8-basic salts obtained by C. Marignac (Ann. Chim. Phys. [4] 3 [1864] 18, 19) on saturation of paratungstate solutions with silicic acid or by neutralisation of the 12-tungstosilicic acid with NH_3, a part is, according to more recent researches by F. Kehrmann and B. Flürscheim (Z. anorg. Ch. 39 [1904] 98), A. Rosenheim and J. Jaenicke (Z. anorg. Ch. 101 [1917] 246) and E. Brauer (Über die Beständigkeit der Anionen der Heteropolysäuren, Dissert., Berlin, 1918, 11), exactly similar to the product obtained by treatment of the 4-basic salts with alkali carbonate, and must be regarded as containing salts of the 10-tungstosilicic acid.

Yet the 8-basicity, founded on the Miolati-Rosenheim theory, was not questioned, for there exists an 8-basic guanidine salt,

$(CN_3H_6)_8\left[Si(W_2O_7)_6\right]6H_2O$ - See R. Haeberle (Zur Kenntnis der Heteropolywolframate, Dissert.,

Berlin, 1911, 36), A. Rosenheim and J. Jaenicke (loc. cit., 344).

Also, systematic researches on the decomposition of the 12-tungstosilicic acid with KOH have shown that, on addition of 10 molecules of KOH to 1 molecule of acid, no decomposition takes place; the possibility of forming an 8-basic potassium salt has also been discussed - A. G. Scroggie and G. L. Clark (Pr. nat. Acad. Washington, 15 [1929] 2).

The 8-basicity is also unchallenged by H. Copaux (Z. anorg. Ch. 74 [1912] 356, 363; Ann. Chim. Phys. [8] 26 [1912] 31, 40; Compt. rend. 156 [1913] 72; Bl. Soc. chim. [4] 13 [1913] 324), but a double basicity is assumed, and expressed by writing the formula $H_4H_4\left[Si\ (W_2O_7)_6\right] \times H_2O$.

cf. E. O. North, G. D. Beal (J. Am. pharm. Assoc. 13 [1924] 892).

This description of the tungstosilicates indicates what one might expect of the tungstotitanates; yet, peculiarly enough, the preparation of the latter compounds was attended, from the commencement, by a difficulty of which no mention is made in the literature which deals with the synthesis of the tungstosilicic acids.

The difficulty referred to is metatungstic acid, $H_{10}\left[H_2(W_2O_7)_6\right] \times H_2O$, which is isomorphous with tungstosilicic and other heteropoly-acids.

All the earlier preparations of tungstotitanic acid contained this isomorphous acid. In order, therefore, to make clear

the difficulties experienced in preparing pure tungstotitanic acid, it becomes necessary to interpose, at this stage, a brief description of the formation, preparation and properties of metatungstic acid.

I. 137-140

Metatungstic Acid.

Historical.

The first data concerning the soluble modification of tungstic acid described by A. Laurent (Ann. Chim. Phys. [3] 21 [1847] 63) as metatungstic acid are those of J. Persoz (Compt. rend. 34 [1852] 135), W. Lotz (Lieb. Ann. 91 [1854] 51) and A. Riche (Ann. Chim. Phys. [3] 50 [1857] 43).

The first thorough investigation of metatungstic acid was undertaken by C. Scheibler (J. pr. Ch. 83 [1861] 310).

Composition, Constitution and Basicity.

The composition of the free acid $H_2O.4WO_3 \cdot x\ H_2O$ or $H_2W_4O_{13} \cdot x\ H_2O$ corresponding to the metatungstates $R_2O.4WO_3 \cdot x\ H_2O$ cannot satisfactorily be established by analysis, for the free acid decomposes very readily. In the literature, the following formulae are given:

$H_2W_4O_{13}.8H_2O$	C. Scheibler (J. pr. Ch. 83 [1861] 310). A. Rosenheim, F. Kohn (Z. anorg. Ch. 69 [1911] 254).
$H_2W_4O_{13}.8.5\ H_2O$	H. Copaux (Ann. Chim. Phys. [8] 17 [1909] 251).
$H_2W_4O_{13} \cdot 9H_2O$.....	M. Sobolew (Z. anorg. Ch. 12 [1896] 28).

A. Rosenheim and F. Kohn (loc. cit.) also prepared the less-heavily hydrated compound $H_2W_4O_{13}.6H_2O$.

C. Scheibler (loc. cit.) made the important observation that a part of the water of crystallisation is necessary for the existence of the molecule and that the entirely dehydrated insoluble residue has lost the characteristic properties of metatungstic acid.

Metatungstic acid is therefore considered to be a compound with a water-containing complex anion (12-tungstoaquic acid), and its relationship with the ordinary heteropoly-acids is expressed by the formulation $H_{10}\left[H_2(W_2O_7)_6\right]$; that the acid never forms deca-basic but only hexa-basic salts is explained by the instability of the anion.

As a result of these considerations, A. Rosenheim and J. Jaenicke (Z. anorg. Ch. 77 [1912] 246) suggested that the hydrated acid could best be represented by the formula

$$H_{10}\left[H_2(W_2O_7)_6\right].\ 22H_2O.$$

and H. Copaux (Ann. Chim. Phys. [8] 17 [1909] 253) supported this view by observing that metatungstic acid is isomorphous with the hydrate $H_8\left[Si(W_2O_7)_6\right].\ 22H_2O$.

Formation.

Metatungstic acid can be prepared from metatungstates by any of the following methods:

1. Decomposition of a solution of ammonium metatungstate with chloroplatinic acid - A. Laurent (Ann. Chim. Phys. [3] 21 [1847] 62).

2. Decomposition of a hot concentrated solution of barium metatungstate with the calculated amount of dilute H_2SO_4 - C. Scheibler (J. pr. Ch. 83 [1861] 310); E. Péchard (Ann. Chim. Phys. [6] 22 1891 198); M. Sobolew (Z. anorg. Ch. 12 [1896] 27); L. Malaprade (Ann. Chim. [10] 11 [1929] 160).

3. Decomposition of a solution of lead metatungstate with H_2S and removal of the excess H_2S by means of a stream of CO_2 - V. Forcher (Ber. Wien Akad. 44, II [1861] 180; J. pr. Ch. 86 [1862] 244); H. Copaux (Ann. Chim. Phys. [8] 17 [1909] 250).

The filtrates obtained by the above methods were evaporated on the water-bath, then in vacuo over H_2SO_4, and so crystallised.

4. Metatungstic acid can also be obtained by the method of Drechsel (Ber. 20 [1887] 1453), by shaking a metatungstate solution with ether and strong acid - M. Sobolew (Z. anorg. Ch. 12 [1896] 29, Note). It was prepared in this way by A. Rosenheim and F. Kohn (Z. anorg. Ch. 69 [1911] 253) from a concentrated aqueous solution of ammonium metatungstate by treatment with ether and strong HCl: this gave a solution containing three layers. The bottom layer - a yellow oil - contained metatungstic acid + ether and some HCl. On evaporation, this yellow oil gave a white crystalline specimen of metatungstic acid which was comparatively stable.

Note.

For each of these preparations a metatungstate is neces-

sary: ammonium metatungstate is the most convenient and may be prepared by the following methods:

(a) Saturation of a boiling solution of ammonia or ammonium tungstate with tungstic acid. After cooling and removing excess tungstic acid by filtration, the ammonium metatungstate was crystallised from the filtrate - M. Marguerite (Ann. Chim, Phys.[3] 17 [1846] 477; J. pr. Ch. 35 [1845] 247).

(b) From a solution of ammonium paratungstate which had been boiled for more than an hour, a part of the salt crystallized unchanged on cooling; but on evaporation of the filtrate to a syrup, ammonium metatungstate separated - A. Laurent (Ann. Chim, Phys. [3] 21 [1847] 62).

Preparation.

The above syntheses of metatungstic acid are very laborious. The following was found to be simpler:

25 gm. sodium tungstate dissolved in 200 c.c. boiling water, and dilute H_2SO_4 added, drop by drop, with stirring, until the solution was just acid to litmus. 3 gm. NaF, dissolved in 100 c.c. of hot water, was added and the mixture well stirred. To this solution, which was kept heated on the waterbath, 20 c.c. of dilute H_2SO_4(5N.) was slowly added, drop by drop, the addition taking about an hour. The solution was boiled for another hour then allowed to cool.

Extracted with ether and 12N.H_2SO_4.

This gave a yellow oil containing metatungstic acid.

Note.

Though this preparation is given here it was actually discovered during work on tungstotitanic acid; and indeed the formation of metatungstic acid, on acidification of a para-tungstate solution containing fluoride, was directly responsible for a great deal of the trouble experienced during the earlier attempts to prepare tungstotitanic acid. This difficulty will again be referred to (See preparation of tungstotitanic acid, p. 47).

Properties.

Separates in clear, colourless crystals, which, in air, quickly effloresce and fall to a powder - M. Sobolew (Z. anorg. Ch. 12 [1896] 28); H. Copaux (Ann. Chim. Phys. [8] 17 [1909] 250).

The stability of different preparations varies greatly: many quickly undergo decomposition in water; others are stable for months. So long as the acid dissolves in water to give a clear solution, it is to be considered as undecomposed - A. Rosenheim and F. Kohn (Z. anorg. Ch. 69 [1911] 254). On heating above 50° decomposition takes place - M. Sobolew (loc. cit.); A. Rosenheim and F. Kohn (loc. cit.).

Solubility.

Readily soluble in water, the solution giving a strong acid reaction with litmus - C. Scheibler (J. pr. Ch.

83 [1861] 310).

Dilute solutions can be kept, undecomposed, in closed vessels for an indefinite period; very concentrated solutions give, after a time, a white insoluble hydrate. Dilute solutions can also be heated for a longer time and can be evaporated to a certain extent on the waterbath.

On further concentration, the hot solution coagulates like albumen and sheds white, insoluble tungstic acid, which gradually changes to the yellow modification.

Concentrated solutions give, with concentrated H_2SO_4, a white precipitate which redissolves on addition of water - C. Scheibler (J. pr. Ch. 83 [1861] 311).

Non-aqueous Solutions.

The solubility of metatungstic acid in ether (100 c.c.) is given by M. Sobolew (Z. anorg. Ch. 12 [1896] 32):-

Temperature.....	0°	7.8°	18.2°	24.3°
gm. $H_2W_4O_{13}.9H_2O$.....	83.456	88.389	99.660	110.76

When the compound loses part of the water, it will dissolve in ether only when the lost water has been recovered.

Contrary to the above statement, A. Rosenheim and F. Kohn (Z. anorg. Ch. 69 [1911] 256) declare that metatungstic acid is insoluble in ether, as the oily layer (containing ether and metatungstic acid) which separates on shaking a strongly acidified metatungstate solution with ether is probably an oxonium salt of ethyl ether.

Metatungstic acid is soluble in absolute alcohol; but

the solution gives no elevation of the boiling-point and is accordingly regarded as a colloid sol - A. Rosenheim and F. Kohn (loc. cit.).

Salts.

Metatungstic acid yields salts of the type $X_6H_4[H_2(W_2O_7)_6]$, only six of the hydrogen atoms being replaceable.

The metatungstates, with the exception of the mercurous and lead salts, are soluble in water. Cf. W. Lotz. (Lieb. Ann. 9 [1854] 73).

Copaux (Compt. rend. 148 [1909] 633) observed that isomorphism existed between metatungstic acid and the complex heteropoly-acids, boro-, phospho- and silico-tungstic acids; and also between certain salts of these acids, e.g. the ammonium, potassium and barium salts.

PART II.

THE TUNGSTOTITANIC ACIDS.

B. ISOLATION OF TUNGSTOTITANIC ACID (12-).

Tungstotitanic Acid.

Formation.

Tungstotitanic acid is formed in two ways:

(a) By saturation of sodium paratungstate solution with titanic acid:

(b) By addition of potassium fluotitanate to sodium paratungstate solution.

In each case, the solution, after being cooled, filtered and extracted with ether + concentrated HCl or 12N.H_2SO_4*, gives two products:

1. A yellow ethereal oil.
2. A yellow precipitate having the appearance of tungstic acid.

(*This is the method of Drechsel Ber. 20 [1887] 1453 which has been used extensively in the preparation of tungstosilicic and other heteropoly-acids. On addition of ether and strong (12N) acid to an aqueous solution of a heteropoly-tungstate, three layers are formed:

(1) An ether layer:

(2) An acid, aqueous layer:

(3) An oil, consisting of the addition compound of the heteropoly-acid with ether. This oil is very dense and sinks to the bottom of the separating funnel.).

1. Ethereal oil.

Dissolved in hot water, and the solution boiled to remove most of the ether. Made strongly alkaline with NaOH ⟶ white flocculent precipitate.

Filtered.

Precipitate. Redissolved in H_2SO_4 and H_2O_2 added → yellow colour

∴ Titanium present.

Filtrate. Acidified with HCl → bulky yellow precipitate

∴ Tungsten present.

The presence of tungsten was confirmed by the "tungsten-blue" test with Zn and HCl.

2. Yellow precipitate.

Treated with very dilute NaOH - dissolved.

Excess NaOH added → white, flocculent precipitate.

Filtered.

Precipitate. Redissolved in H_2SO_4 and H_2O_2 added → yellow colour

∴ Titanium present.

Filtrate. Acidified with HCl → bulky yellow precipitate

∴ Tungsten present.

The presence of tungsten was confirmed by the "tungsten-blue" test with Zn and HCl.

It appeared, then, that the ethereal oil and the yellow solid each contained both titanium and tungsten; and it was evident that the amount of titanium in the yellow solid was such that it could scarcely be attributed to adsorption.

The yield of oil from several consecutive preparations varied, and it was observed that, in cases where the yield was poor, the amount of yellow solid which separated was considerable.

Tungstotitanic Acid.

Preparation.

(a) Saturation of sodium paratungstate solution with titanic acid.

25 gm. of sodium tungstate dissolved in 200 c.c. of boiling water. Solution made faintly acid to litmus with dilute H_2SO_4. To this hot and well-stirred solution, freshly-precipitated titanic acid was added in small portions. About 10 additions of ·2 gm. of titanic acid were made, at intervals of about 3 hours, each addition being accompanied by 1 c.c. of $3N.H_2SO_4$.

When the saturation had been completed, the solution was filtered and the filtrate extracted with ether and acid. Each preparation by this method required at least a week.

Analysis of oil.

Oil evaporated to dryness in a weighed platinum crucible, and the residue of mixed oxides (TiO_2 + WO_3) weighed.

Fused with Na_2CO_3, cooled, and the melt digested with water.

Titanium-containing residue filtered off, and washed with hot water * until filtrate was neutral to phenol-phthalein to ensure that all the alkali tungstate had been removed.

[* This method of analysis is recommended by Hillebrand (Hillebrand and Lundell, "Applied Inorganic Analysis" [1929] pp. 455, 551); cf. F. A. Gooch (Proc. Am. Acad. Arts and Sci., New Series, 12 [436] 1884-85); W. F. Hillebrand (U.S. Geol. Surv. Bull., 700, p. 132); V. Auger (Compt. rend. 177 [1923] 1302)].

Precipitate treated on filter-paper with 50 c.c. hot 3N.HCl and well washed with hot water.

Filtrate made alkaline to methyl red with NH_4OH and boiled - titanic acid precipitated.

Filtered through the same paper as before. Washed with hot water. Ignited and weighed as TiO_2.

Results.

1. Wt. of mixed oxides ($TiO_2 + WO_3$) = .7392 gm.

Wt. of TiO_2 = .0112 gm.

∴ Wt. of WO_3 (by difference) = .7280 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{22.4}$$

2. Wt. of mixed oxides = .7032 gm.

Wt. of TiO_2 = .0094 gm.

∴ Wt. of WO_3 (by difference) = .6938 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{25.5}$$

If tungstotitanic acid be really analogous to tungstosilicic acid, then, theoretically the ratio should be

$$\frac{TiO_2}{WO_3} = \frac{1}{12}$$

Tungstotitanic Acid.

Preparation.

(b) Addition of potassium fluotitanate to sodium paratungstate solution.

50 gm. sodium tungstate dissolved in 300 c.c. boiling water, and the solution acidified with dilute H_2SO_4. 10 gm. K_2TiF_6, dissolved in boiling water, added. Solution well stirred and evaporated to 250 c.c., allowed to cool, filtered, then extracted with ether and 12N.H_2SO_4.

Analysis of oil.

Method as before (see p. 42).

Result.

Wt. of mixed oxides (TiO_2 + WO_3) = .2386 gm.

Wt. of TiO_2 = .0045 gm.

∴ Wt. of WO_3 (by difference) = .2341 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{17.96}$$

Results from both preparations, (a) and (b), unsatisfactory.

Of the two methods, (b), the potassium fluotitanate preparation, being much more quickly and more easily carried out, was preferable.

It was therefore decided to concentrate on it.

Development of the preparation of tungstotitanic acid from K_2TiF_6.

Note.

This treatment ultimately gave a pure specimen of tungstotitanic acid (12-). In what follows it is important to note that metatungstic acid was present, as impurity, in all the earlier specimens of tungstotitanic acid.

The method was evolved in four stages, of which the following is a summary.

I. - Addition of all the K_2TiF_6 at once.

Analysis of oil.

Results unsatisfactory and yields poor.

Discovery of the preparation of metatungstic acid from tungstate and fluoride. This suggested the preparation of tungstotitanic acid by slow addition of dilute K_2TiF_6 solution to the carefully acidified tungstate solution.

II. - Slow addition of dilute K_2TiF_6 solution to carefully acidified tungstate solution.

Analysis of oil.

Analysis of yellow precipitate - showed that the yellow precipitate was an impure 10-tungstotitanic acid, formed, together with metatungstic acid, on heating the 12-tungstotitanic acid. Hence decided to chill the solution before extraction of the acid.

III. - Slow addition of dilute K_2TiF_6 solution to carefully acidified tungstate solution. Left to stand overnight, chilled and extracted.

Analysis.

Acid now contained too high a proportion of titania, so decided to filter it, then redissolve in alcohol and re-precipitate.

IV. - Slow addition of dilute K_2TiF_6 solution to carefully acidified tungstate solution. Left to stand overnight, chilled and extracted. Oil filtered, redissolved in alcohol and re-precipitated.

Analysis.

Pure specimen of tungstotitanic acid (12-) obtained.

Details of stages I, II, III and IV in the evolution of the preparation of pure 12-tungstotitanic acid are now given:

Stage I.

50 gm. sodium tungstate dissolved in 500 c.c. boiling water. Solution acidified and 10 gm. K_2TiF_6, dissolved in boiling water, was added. Solution stirred continuously and evaporated to 250 c.c. Cooled and filtered. Filtrate extracted with ether and 12 N.H_2SO_4.

Analysis of oil.

Method as before (see p. 42).

Result.

Wt. of mixed oxides (TiO_2 + WO_3)	=	.2643 gm.
Wt. of TiO_2	=	.0044 gm.
∴ Wt. of WO_3 (by difference)	=	.2599 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{20.4}$$

The synthesis of metatungstic acid from sodium tungstate + alkali fluoride (see p. 36) was discovered at this time. Now, if potassium fluotitanate be added to a solution of sodium paratungstate which contains free mineral acid, the latter will react with the potassium fluoride (for potassium fluotitanate can be regarded as $2KF.TiF_4$) liberating hydrofluoric acid, which will then attack the tungstate, forming metatungstic acid.

Thus it appears that, unless care be taken to control the P_H of the reacting tungstate solution, metatungstic acid, as well as tungstotitanic acid, will be formed.

Copaux (Compt. rend. 148 [1909] 633) observed that true isomorphism existed between metatungstic acid and the complex heteropoly acids, boro-, phospho- and silico-tungstic acids; and also between certain salts of these acids, e.g. the ammonium, potassium and barium salts.

Since there is every reason to believe that tungstotitanic acid will be analogous to tungstosilicic acid, and therefore isomorphous with metatungstic acid, the presence of metatungstic acid, as impurity, in a specimen of tungstotitanic acid presents grave difficulties: any attempt to separate the two acids by a crystallisation or precipitation method is likely to be unsatisfactory.

This being so, it becomes necessary so to modify the preparation of tungstotitanic acid that the formation of metatungstic acid will be impossible.

Thus

(a) The presence of free mineral acid in the paratungstate solution is undesirable.

Sodium paratungstate is $5Na_2O.12WO_3$; and, theoretically, 25 gm. of Na_2WO_4 (anhydrous) requires 24.6 c.c. of 4.028 N.H_2SO_4 to convert it to paratungstate.

The solution reacts acid to litmus when 23.8 c.c. of 4.028N.H_2SO_4 have been added.

Hence it was decided that, in future preparations, the sodium tungstate solution should be made just acid to litmus with dilute H_2SO_4, yielding a compound approximating to the composition of paratungstate but containing slightly more alkali. This would give a narrow, but ample, margin of safety and ensure that the starting material was adjusted to a suitable P_H.

(b) Consider, now, the reaction between sodium paratungstate and potassium fluotitanate. It is difficult to write an equation representing exactly what happens, but the following is probably a fair approximation:

$$5Na_2O.12WO_3 + 2K_2TiF_6 + 2H_2O = Na_4H_4[Ti(W_2O_7)_6] + 6NaF + 4KF + TiOF_2$$

(assuming that tungstotitanic acid forms compounds of types similar to the tungstosilicates).

Of all the compounds originally taking part in, or subsequently produced by, this reaction, potassium fluotitanate alone is strongly acidic.

The reaction takes place slowly.
Thus, if all the potassium fluotitanate required for formation of tungstotitanate be added at one time, the solution must inevitably become more acid.

If, however, the K_2TiF_6 be so added that the rate of addition does not exceed the rate at which K_2TiF_6 reacts with sodium paratungstate, the P_H of the solution should remain approximately the same until all the tungstate has been converted to tungstotitanate.

Considerations (a) and (b) resulted in Stage II, given below.

Stage II.

25 gm. sodium tungstate dissolved in 150 c.c. of boiling water. Solution made just acid to litmus with dilute H_2SO_4. 5 gm. K_2TiF_6 was dissolved in 400 c.c. boiling water. The paratungstate solution was kept heated and stirred while the hot fluotitanate solution was dropped in from a small funnel with a capillary jet, which delivered about 1 drop per second.

When all the fluotitanate had been added, the solution was cooled, filtered, and the filtrate extracted with ether and 12N.H_2SO_4.

Analysis of oil.

Method as before (see p. 42).

Results.

1. Wt. of mixed oxides (TiO_2 + WO_3) = 1.8327 gm.

Wt. of TiO_2 = .0468 gm.

∴ Wt. of WO_3 (by difference) = 1.786 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{13.2}$$

---

2. Wt. of mixed oxides = 2.3343 gm.

Wt. of TiO_2 = .0606 gm.

∴ Wt. of WO_3 (by difference) = 2.274 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{13.0}$$

Results show a great improvement, but the proportion of titania in the compound is still slightly low.

There was reason to suspect that the yellow precipitate, which was invariably produced during extraction, had some connection with this error, so a sample of the precipitate was analysed.

Analysis.

Method as for the analysis of the oil (see p. 42).

Result.

Wt. of mixed oxides ($TiO_2 + WO_3$) = .5865 gm.

Wt. of TiO_2 = .0177 gm.

$\therefore$ Wt. of WO_3 (by difference) = .5688 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{11.1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

This yellow powder might be a decomposition-product of the tungstotitanic acid oil.

Some of the oil was therefore dissolved in water and heated with strong HCl. This gave a yellow precipitate, which was filtered and analysed.

Analysis.

Method as before (see p. 42).

Result.

Wt. of mixed oxides ($TiO_2 + WO_3$) = .9308 gm.

Wt. of TiO_2 = .0289 gm.

$\therefore$ Wt. of WO_3 (by difference) = .9019 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{10.8} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The results of these two analyses indicate that the yellow precipitate consists of a solid 10-tungstotitanic acid plus a small amount of tungstic acid.

Also, the method of preparation used in the case of specimen (2) shows quite definitely:

(a) That the solid 10-tungstotitanic acid is formed by decomposition of the ethereal oil in acid solution.

(b) That this decomposition is accelerated by heat.

Specimen (2) of the yellow solid was obtained by heating the ethereal oil with strong HCl.

This specimen of oil was prepared by the Stage I method (p. 46), i.e. the ratio for $\frac{TiO_2}{WO_3}$ is approximately $\frac{1}{20}$.

(This was verified by several further analyses which showed that $TiO_2:WO_3 \fallingdotseq 1:20$ was correct for oils prepared by this method).

Thus:

A yellow solid (in which $\frac{TiO_2}{WO_3} = \frac{1}{11}$) is formed by decomposition of an oil (in which $\frac{TiO_2}{WO_3} = \frac{1}{20}$). It follows that formation of the yellow solid must result in an accumulation of tungstic acid in the mother-liquor; and the only water-soluble form of tungstic acid is <u>metatungstic acid</u>.

The equation for the decomposition may therefore be expressed thus:

$$H_8[Ti(W_2O_7)_6] = H_8[TiO(W_2O_7)_5] + 2WO_3$$

12-tungstotitanic acid — 10-tungstotitanic acid.

(Assuming that the oil, like tungstosilicic acid, contains 12-tungstotitanic acid).

The molecules of WO_3, of which two are liberated by decomposition of each molecule of 12-tungstotitanic acid, link up to form metatungstic acid, $H_{10}[H_2(W_2O_7)_6]$.

Since decomposition of 12-tungstotitanic acid, with formation of metatungstic acid, takes place on warming the acid solution, it was decided that, in future, the solution must be chilled before commencing to extract the acid.

This was carried into practice in Stage III.

Stage III.

25 gm. of sodium tungstate dissolved in 150 c.c. boiling water. Solution made just acid to litmus with dilute H_2SO_4. 5 gm. of K_2TiF_6 dissolved in 400 c.c. boiling water. The paratungstate solution was kept heated and stirred while the hot fluotitanate solution was added from a small dropping-funnel with a capillary jet, which delivered about one drop per second.

When all the fluotitanate had been added, the solution was allowed to cool overnight* and filtered.

Filtrate, chilled in a freezing-mixture of ice and salt, was extracted with ether and 12 N.H_2SO_4.

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* It is advisable to leave the solution to cool overnight. This allows cooling to take place slowly and ensures that the

sodium tungstotitanate shall be fully hydrated. Rapid cooling of the solution may tend to give a sodium tungstotitanate which does not contain its full complement of co-ordinated water molecules.

Analysis.

Method as before (see p. 42).

Results.

1. Wt. of mixed oxides ($TiO_2 + WO_3$) = 1.0354 gm.
   Wt. of TiO_2 = .0316 gm.
   ∴ Wt. of WO_3 (by difference) = 1.004 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{10.96}$$

---

2. Wt. of mixed oxides = 1.1110 gm.
   Wt. of TiO_2 = .0354 gm.
   ∴ Wt. of WO_3 = 1.076 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{10.5}$$

These analyses show that the oil now contains too high a proportion of titania. Hence it was decided to filter the oil through a cotton-wool plug, dissolve in absolute alco-

hol then re-precipitate from ether. This should free the oil from any trace of titanium-containing precipitate and from any drops of aqueous mother-liquor (See Stage IV).

Stage IV.

25 gm. of sodium tungstate dissolved in 150 c.c. of boiling water. Solution made just acid to litmus with dilute H_2SO_4. 5 gm. of K_2TiF_6 dissolved in 400 c.c. of boiling water. The paratungstate solution was kept heated and stirred while the hot fluotitanate solution was added from a small dropping-funnel with a capillary jet, which delivered about one drop per second.

When all the fluotitanate had been added, the solution was allowed to cool overnight and filtered.

Filtrate (vol. 200 c.c.) chilled in a freezing mixture of ice and salt.

Extracted with 80 c.c. ether + 250 c.c. 12N.H_2SO_4. Ethereal oil filtered through a cotton-wool plug, dissolved in absolute alcohol and re-precipitated by addition of ether to the alcohol.

Analysis.

Up to this point, the method of analysis used (i.e. fusion of the mixed oxides with Na_2CO_3 and estimation of the TiO_2, $-WO_3$ being obtained by difference) had been quick and reasonably accurate. Since the acid now prepared seemed likely to be very nearly pure, a full analysis was made, thus:

100-150 drops of oil dissolved in 100 c.c. of water. Solution made strongly alkaline with NaOH - titania precipitated.

Filtered and washed with hot water.

Precipitate. Redissolved in hot, dilute HCl and re-precipitated with NH_4OH. Ignited and weighed as TiO_2.

Filtrate. Tungsten precipitated as mercurous tungstate.

Ignited and weighed as WO_3.

Results.

1. Wt. of TiO_2 = .0168 gm.
   Wt. of WO_3 = .6180 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{12.7}$$

2. Wt. of TiO_2 = .0188 gm.
   Wt. of WO_3 = .6889 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{12.7}$$

Although the theoretical result should be $\frac{TiO_2}{WO_3} = \frac{1}{12}$, in view of the fact that no really accurate method is known for the estimation of titanium in presence of tungsten,

these results are very satisfactory. They indicate that the method used in Stage IV yields a product which is virtually pure 12-tungstotitanic acid, $H_8[Ti(W_2O_7)_6]$.

12-Tungstotitanic Acid.

Formation. } Already described (See pp. 40-55).
Preparation. }

Properties.

The stability of the acid is rather less than that of metatungstic acid. On account of this, it has not yet been possible to obtain a crystalline specimen of the compound.

Evaporation of the ethereal oil, in the cold, yields a yellowish solid, which contains a good deal of insoluble 10-tungstotitanic acid - clear evidence of decomposition.

Aqueous solutions of the acid react in at least two ways:

1. On heating. A white precipitate containing a relatively high proportion of titania is obtained.
2. On heating with HCl. A yellow precipitate of 10-tungstotitanic acid plus a small amount of tungstic acid is obtained.

Theoretically it should be possible to form almost any salt of tungstotitanic acid by addition of the hydroxide or carbonate of the appropriate metal.

In practice this cannot be done.

The only means of determining the amount of acid in the viscous ethereal oil is to estimate the titanium and tungsten contained in a known number of drops of the oil. This method of counting the drops will, obviously, give only a rough approximation to the real volume of the oil; and, as excess alkali decomposes the acid (and neutralisation must therefore be exact) the salts cannot be obtained in this way.

It is, of course, an easy matter to estimate the amount of tungstotitanic acid in, say, 25 c.c. of the aqueous solution; but the estimation requires two days. As the aqueous solution is unstable, neutralisation would have to be carried out immediately; so this method is not available for the preparation of salts.

In the case of insoluble carbonates neutralisation might be possible. The barium salt has been prepared by addition of a paste, consisting of finely-ground $BaCO_3$ and water, to the cooled aqueous solution of tungsto-titanic acid. A mixture of barium tungstate and barium tungstotitanate was formed (see p. 66).

SALTS.

Ammonium tungstotitanate.

Preparation.

Ammonium tungstotitanate was prepared by saturation of ammonium paratungstate solution with freshly-precipitated titanic acid. The crude ammonium tungstotitanate was dissolved in 50 c.c. of water and equal volume of saturated NH_4Cl solution added - precipitate formed.

Precipitate (ammonium paratungstate) filtered off.

Ammonium paratungstate appears to be formed by decomposition of ammonium metatungstate, and can be completely salted-out by addition of NH_4Cl. Hence this treatment gives a filtrate which is free from metatungstate.

Filtrate.

Acidified carefully with concentrated HCl.
Very slowly, a brownish-white precipitate of ammonium tungstotitanate separated. Precipitate filtered off, redissolved in boiling water, filtered and recrystallised. This gave a yellowish-white, microcrystalline compound.

The yield was extremely poor: from about 25 gm. of crude ammonium tungstotitanate only about $1\frac{1}{2}$ gm. of recrystallised salt was obtained.

Analysis.

Method.

Salt placed in a weighed platinum crucible and heated in the electric furnace to 500°C. Residue of mixed oxides

(TiO_2 + WO_3) fused with Na_2CO_3 and melt extracted with water - titania precipitated.

Precipitate. Filtered and thoroughly washed with hot water. Filter-paper + precipitate treated with 50 c.c. of hot 3N.HCl to redissolve the titania. Paper washed with hot water. Titanium hydroxide re-precipitated by addition of NH_4OH to the solution until just alkaline to methyl red.

Precipitate washed with hot water.

Ignited and weighed as TiO_2.

Results.

1. Wt. of mixed oxides (TiO_2 + WO_3) = .6855 gm.
   Wt. of TiO_2 = .0238 gm.
   ∴ Wt. of WO_3 (by difference) = .6617 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{9.6}$$

---

2. Wt. of mixed oxides = .5093 gm.
   Wt. of TiO_2 = .0173 gm.
   ∴ Wt. of WO_3 = .4920 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{9.8}$$

Now all the ammonium salts of tungstosilicic acid are derivatives of the 10-acid, $H_8[SiO(W_2O_7)_6]$ - see the following references:

A. Riche (Ann. Chim. Phys. [3] 50 [1857] 62).

C. Marignac (Ann. Chim. Phys. [3] 69 [1863] 83, 85, 86; [4] 3 [1864] 17, 18, 59, 60).

G. Wyrouboff (Bl. Soc. Min. 19 [1896] 239).

A. Pinagel (Beiträge zur Kenntnis der Wolframate und Silicowolframate, Dissert., Berlin, 1904).

F. Kehrmann, R. Flührscheim (Z. anorg. Ch. 39 [1904] 98, 101).

H. Copaux (Bl. Soc. Chim. [4] 3 [1908] 108).

A. Rosenheim, J. Jaenicke (Z. anorg. Ch. 101 [1917] 245-247).

E. O. North, G. D. Beal (J. Am. pharm. Assoc. 13 [1924] 894).

Hence, by analogy, the ratio $\frac{TiO_2}{WO_3}$ in ammonium tungstotitanate should be $\frac{1}{10}$.

This agrees very well with the results of the analysis, and there can be no doubt that the ammonium tungstotitanate obtained is a salt of the 10-acid, $H_8[TiO(W_2O_7)_5]$.

So far, it has been impossible to prepare this ammonium salt in sufficient quantity to carry out an estimation of the ammonia and water as well as the titanium and tungsten.

Ammonium tungstosilicate, $(NH_4)_3H_5[SiO(W_2O_7)_5]$ was prepared by heating the normal salt with HCl - C. Marignac (Ann. Chim. Phys. [3] 69 [1863] 86; [4] 3 [1864] 18); G. Wyrouboff (Bl. Soc. Min. 19 [1896] 239).

But ammonium tungstotitanate cannot be heated with HCl, otherwise the solid 10-tungstotitanic acid is precipitated. The solution must therefore be left to stand in the cold. This results in a very poor yield; for, even in the cold, the salt decomposes slowly, and after two or three days the 10-acid makes its appearance, indicating that decomposition is well advanced.

Further research will be necessary to discover whether it is possible to alter the method of preparation so that 10-tungstotitanic acid will not be precipitated.

It appears, then, that the compound is undoubtedly an ammonium tungstotitanate (10-), but the full formula, in terms of NH_4, H and H_2O groups cannot yet be given. It is probably the titanium analogue of $(NH_4)_3\ H_5\left[SiO(W_2O_7)_5\right]$.

Potassium Salt.

Potassium tungstosilicate $K_3H_5\left[Si(W_2O_7)_6\right]\ 12\frac{1}{2}\ H_2O$ has been prepared by concentrating the H_2SO_4 solution of $K_4H_4\left[Si(W_2O_7)_6\right]\cdot 16\ H_2O$. But the salt is unstable and decomposes in water - C. Marignac (Ann. Chim. Phys. [4] 3 [1864] 21); G. Wyrouboff (Bl. Soc. Min. 19 [1896] 252; Z. Kryst. 29 [1898] 663).

The preparation of potassium tungstotitanate was attempted

(a) By saturation of crude potassium tungstotitanate with KCl,

filtration of the precipitate and acidification of the filtrate with HCl.

(b) By saturation of an aqueous solution of tungstotitanic acid (12-) with KCl.

In each case the salt formed was decomposed by water and could not be re-crystallised for analysis.

Guanidine Salt.

Preparation.

Tungstotitanic acid, which had given, on analysis, the ratio $\frac{TiO_2}{WO_3} = \frac{1}{12.7}$ was used as starting material.

The ethereal solution of the acid (about 20 c.c.) was dissolved in 50 c.c. of water and a solution of guanidine hydrochloride added, drop by drop, till no further precipitate appeared. The precipitate was filtered, well drained and analysed.

Analysis.

The salt was placed in a weighed platinum crucible and heated in the electric furnace at 500°C.

Residue of $TiO_2 + WO_3$ weighed.

Fused with Na_2CO_3 and melt extracted with hot water - titania precipitated.

Precipitate. Filtered and washed with hot water.

Filter-paper + precipitate treated with 50 c.c. of hot 3 N.HCl to redissolve the titania. Paper thoroughly washed with hot water.

Filtrate made just alkaline to methyl red with NH_4OH - titanium hydroxide precipitated. Filtered, washed with hot water, ignited and weighed as TiO_2.

Result.

1. Wt. of mixed oxides (TiO_2 + WO_3) = 1.8039 gm.
   Wt. of TiO_2 = .0538 gm.
   ∴ Wt. of WO_3 (by difference) = 1.7501 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{11.23}$$

A second analysis was carried out. The method was the same as before, with the exception that the titania residue from the extraction of the sodium carbonate melt, after being well washed with hot water, was dissolved in concentrated HCl (filter-paper + precipitate placed in a beaker with 30 c.c. concentrated HCl and heated for 10 minutes on the waterbath).

This made quite certain that all the titanium residue was dissolved, and consequently gave a better analysis.

Result:

2. Wt. of mixed oxides (TiO_2 + WO_3) = 2.0330 gm.
   Wt. of TiO_2 = .0575 gm.
   ∴ Wt. of WO_3 (by difference) = 1.976 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{11.87}$$

These analyses indicate that the compound is a guanidine salt of 12-tungstotitanic acid, $H_8[Ti(W_2O_7)_6]$.

The compound was recrystallised from water and dried in vacuo over calcium chloride, in the hope of obtaining a pure specimen which could be subjected to a complete analysis for titanium, tungsten, guanidine and water.

But the result given below for the determination of the $\frac{TiO_2}{WO_3}$ ratio shows that the salt has decomposed during recrystallisation.

Result.

Wt. of mixed oxides (TiO_2 + WO_3)	=	1.5132 gm.
Wt. of TiO_2	=	.0374 gm.
∴ Wt. of WO_3 (by difference)	=	1.476 gm.

This gives the ratio:

$$\frac{TiO_2}{WO_3} = \frac{1}{13.6}$$

The behaviour of the acid ammonium and guanidine salts of tungstotitanic acid suggests:

(a) That some, at least, of the acid salts of tungstotitanic acid can be prepared from a mother-liquor containing free tungstotitanic acid.

(b) That when such an acid salt is redissolved in water, a new equilibrium is set up, liberating free tungstotitanic acid from the acid salt (and this free acid, being unstable,

causes progressive decomposition of the salt through continuous disturbance of the equilibrium).

Even the more basic barium salt can only be recrystallised unchanged from its own mother-liquor. Recrystallisation from water alone causes partial decomposition.

Barium Salt.

1st Preparation.

The oily addition compound of tungstotitanic acid with ether was used as starting-material. This was treated with excess $BaCO_3$ ground to a fine powder and suspended in water. Left overnight in the thermostat at 33°C.

Solid matter filtered off, warmed with acetic acid, and filtered. This removed the barium carbonate.

The residue was extracted with hot water, filtered, and the filtrate concentrated to moderate bulk, separated from any trace of barium tungstate, and further concentrated.

The crystals which separated were dried in air.

The salt is micro-crystalline, colourless, and very sparingly soluble in water.

Analysis.

The salt was placed in a weighed platinum crucible, ignited at 700°C. and weighed.

Fused with Na_2CO_3 and the melt extracted with hot water.

Residue contained $BaCO_3$ + titania and some tungsten.

Solution contained most of the sodium tungstate.

Residue washed with Na_2CO_3 solution, and the washings added to the tungsten filtrate.

Residue then treated with hot, dilute HCl - this dissolved the $BaCO_3$ and most of the titania; but some titania remained undissolved.

Undissolved residue:

Ignited in a platinum crucible and once more fused with Na_2CO_3. Melt extracted with hot water and the residue filtered and washed with Na_2CO_3 solution.

Filtrate and washings added to the main tungsten filtrate.

Residue:

Redissolved by washing with hot, dilute HCl, and added to the previous HCl solution.

The combined HCl washings were treated with dilute H_2SO_4 to precipitate the barium as sulphate. This was filtered off.

The filtrate was made alkaline to methyl red with NH_4OH - titanium hydroxide precipitated. Ignited and weighed as TiO_2.

The combined tungsten filtrates and washings were diluted to 500 c.c., 150 c.c. of this solution taken, and the tungsten precipitated as mercurous tungstate. Ignited and weighed as WO_3.

Results:

Wt. of salt used = 1.0444 gm.

Wt. of residue on ignition = .8974 gm.

Wt. of $BaSO_4$ obtained = .2332 gm.

Wt. of TiO_2 " = .0246 gm.

Wt. of WO_3 " = .7196 gm.

Wt. of H_2O (by ignition loss) = .1470 gm.

i.e.

Oxide.	% (Found).	% (Theor.).	Formula.
BaO	14.67	13.81	
TiO_2	2.35	2.40	$3BaO.TiO_2.10WO_3.26H_2O.$
WO_3	68.90	69.71	
H_2O	14.08	14.06	

Barium Salt.

2nd Preparation.

The free acid was treated with a large excess of saturated barium chloride solution and evaporated in vacuo. The successive small crops of crystals were removed as they separated, and the evaporation continued until barium chloride started to crystallise.

The various crops of crystals were then combined and recrystallised from water. This gave two fractions (together with a small residue of barium tungstate):

(a) A colourless, well-crystallised salt which was readily soluble in water:

(b) A colourless salt, micro-crystalline and sparingly soluble in water.

Fraction (a) was analysed.

Analysis.

Method as for the previous barium salt (p. 66).

Results.

Wt. of salt used	=	1.1322 gm.
Wt. of residue on ignition	=	1.0316 gm.
Wt. of $BaSO_4$ obtained	=	.2442 gm.
Wt. of TiO_2 "	=	.0280 gm.
Wt. of WO_3 "	=	.8431 gm.
Wt. of H_2O (by ignition loss)	=	.1006 gm.

i.e.

Oxide.	% (Found).	% (Theor.).	Formula.
BaO	14.18	14.62	
TiO_2	2.47	2.54	
WO_3	74.47	73.70	$3BaO.TiO_2.10WO_3.16H_2O$.
H_2O	8.88	9.15	

Barium Salt.

3rd Preparation.

25 gm. of sodium tungstate dissolved in 150 c.c. of boiling water. Solution made just acid with HNO_3.

5 gm. of K_2TiF_6 dissolved in 400 c.c. of boiling water. The paratungstate solution was kept heated and well-stirred while the hot fluotitanate solution was added from a small dropping-funnel with a capillary jet, which delivered one drop per second.

When all the fluotitanate had been added, the solution was allowed to cool overnight, then filtered.

To the filtrate 25 c.c. of saturated barium chloride solution was added and the mixture set aside for 12 hours - precipitate formed.

Precipitate (contains BaF_2 + barium tungstotitanate):

Filtered off, extracted with hot water, and the hot extract again filtered.

The crystals which separated from this solution were

dried in air.

The salt is well-crystallised, faintly violet, and moderately soluble in water.

Analysis.

Method as before (p. 66).

Results:

Wt. of salt used	=	1.2796 gm.
Wt. of residue on ignition	=	1.1114 gm.
Wt. of $BaSO_4$ obtained	=	.2738 gm.
Wt. of TiO_2 "	=	.0331 gm.
Wt. of WO_3 "	=	.9002 gm.
Wt. of H_2O (by ignition loss)	=	.1682 gm.

i.e.

Oxide.	% (Found).	% (Theor.)	Formula.
BaO	14.06	13.97	$3BaO.TiO_2.10WO_3.24H_2O.$
TiO_2	2.45	2.43	
WO_3	70.35	70.47	
H_2O	13.14	13.13	

PART III.

THE HETEROPOLY-TUNGSTIC ACIDS IN GENERAL.

An entirely new series of heteropoly-tungstic acids has been prepared: these compounds are formed by combination of tungstic oxide with the oxides of such elements as

Ag, Cu, Zn, Ti, Zr, V, Nb, Ta, Cr, Mo, Cl, Fe.

Before discussing the significance of these compounds, the methods used for their preparation will be given.

Tungstoargentic Acid.

Preparation.

4 gm. $AgNO_3$ } dissolved in 300 c.c. water.
3 gm. NaF. }

20 gm. Na_2WO_4

The sodium tungstate was dissolved in 100 c.c. of boiling water and the solution made faintly acid to litmus with dilute H_2SO_4. The solution was heated, stirred and the silver nitrate-sodium fluoride mixture added from a dropping-funnel with a capillary jet.

Gradually a white precipitate formed (possibly silver paratungstate).

After all the silver nitrate had been added the solution was stirred and heated for a further 30 minutes.

The precipitate appeared to dissolve in part.

5 c.c. of 5N.H_2SO_4 then added, a drop at a time, with stirring.

Solution filtered and the filtrate (vol. 200 c.c.) chilled in a freezing mixture and 80 c.c. ether stirred in. Then 250 c.c. of 12N.H_2SO_4 was added from a dropping-funnel, the solution being stirred continuously and the acid added slowly.

An ethereal oil separated.

Test.

Oil dissolved in water and heated on waterbath to remove most of the ether.

Solution made strongly alkaline with NaOH - brown colour - silver hydroxide separated slowly on standing.

The aqueous solution of the oil gave no precipitate with NaCl, NaBr or NaI; neither did it give any precipitate with H_2S. But the presence of silver was confirmed thus:

The ammoniacal solution of the oil was treated with an acetone solution of p-dimethylamino-benzal-rhodanine (See B. D. H. Book of Reagents, No. 7, p. 21).

This gave a reddish-brown precipitate, ∴ Ag present.

Hence the oil contains tungstoargentic acid.

Tungstocupric Acid.

Preparation.

5 gm. $CuSO_4.5H_2O$.

3 gm. NaF.

25 gm. Na_2WO_4.

The sodium tungstate was dissolved in 100 c.c. boiling water and the solution made just acid to litmus with dilute H_2SO_4. The sodium fluoride was added, and the solution heated and well stirred. The copper sulphate, dissolved in 300 c.c. of water, was run in from a funnel with a capillary jet which delivered about one drop per second.

A greenish precipitate gradually formed (possibly copper paratungstate) but as the latter part of the copper sulphate solution was added, the precipitate appeared to re-dissolve in part.

After all the copper sulphate had been added, the solution was boiled for a further 30 minutes. Left to stand overnight and filtered. Filtrate (vol. 200 c.c.) chilled and stirred, then added 80 c.c. ether followed by 250 c.c. $12N.H_2SO_4$.

A pale-green oil separated.

Test.

The oil was dissolved in water and heated to remove most of the ether.

Solution made strongly alkaline with NaOH - green precipitate, $\therefore$ Cu present.

Hence the oil contains tungstocupric acid.

Tungstozincic Acid.

Preparation.

5 gm. $ZnSO_4.7H_2O$.

25 gm. Na_2WO_4.

The sodium tungstate was dissolved in 100 c.c. boiling water and the solution made just acid to litmus with dilute H_2SO_4.

The zinc sulphate was dissolved in 100 c.c. water and the solution made just alkaline with NaOH. The aqueous suspension of $Zn(OH)_2$ thus obtained was added, in small portions, to the hot paratungstate solution, the latter being kept just acid by addition of dilute H_2SO_4.

The solution was allowed to cool overnight. Filtered and the filtrate (vol. 200 c.c.) extracted with ether and 12N.H_2SO_4 from chilled solution - an oil separated.

Test.

Oil dissolved in water and the solution heated to remove most of the ether.

Solution made strongly alkaline with NaOH - white precipitate which dissolved in excess NaOH.

Alkaline solution saturated with H_2S - white precipitate, ∴ Zn present.

Hence the oil contains tungstozincic acid.

Tungstozirconic Acid.

Preparation.

5 gm. potassium fluozirconate.

25 gm. sodium tungstate.

The method of preparation used was exactly similar to that of tungstotitanic acid.

Test.

Oil dissolved in water and the solution heated to remove most of the ether.

Solution made strongly alkaline with NaOH - white precipitate, ∴ Zr present.

Hence the oil contains tungstozirconic acid.

Tungstoniobic Acid.

(1) Preparation from potassium oxyfluoniobate and sodium tungstate.

20 gm. of sodium tungstate dissolved in 100 c.c. hot water.

Solution made just acid to litmus with H_2SO_4, heated and stirred.

4 gm. of potassium oxyfluoniobate, dissolved in 200 c.c. boiling water, was slowly added. Solution left to stand overnight, filtered and extracted with ether and 12N.H_2SO_4.

An oil separated.

(2) Preparation from sodium niobate and sodium tungstate.

20 gm. of sodium tungstate dissolved in 100 c.c. hot water.

Solution made just acid to litmus with H_2SO_4.

The sodium niobate (5 gm.), dissolved in 150 c.c. boiling water, was slowly added, and the mixture heated on the water-bath and stirred.

H_2SO_4(5N.) run in carefully, drop by drop, until the mixture reacted acid to litmus.

Left to stand overnight.

Solution divided into two parts:

(a) Chilled and extracted with ether and 12 N.H_2SO_4 - bulky precipitate formed, but no ethereal oil.

(b) 2 gm. NaF added. Chilled and extracted with ether and 12 N.H_2SO_4 - oil separated.

Tests.

(1) Oil prepared from potassium oxyfluoniobate and sodium tungstate was dissolved in hot water.

Solution made strongly alkaline with NaOH, NH_4Cl added and boiled - white precipitate.

Precipitate filtered and washed with water until the filtrate was neutral to phenol phthalein. Redissolved in a hot solution of oxalic acid, tannin added, and the whole "buffered" with ammonium acetate and heated - red precipitate,

∴ Nb present.

Hence the oil contains tungstoniobic acid.

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(2) Oil prepared from sodium niobate and sodium tungstate + sodium fluoride was tested in the same way, and gave the same result.

Tungstotantalic Acid.

Preparation.

2.5 gm. K_2TaF_7.

15 gm. Na_2WO_4.

The sodium tungstate was dissolved in 50 c.c. hot water, the solution made just acid to litmus with H_2SO_4, heated and stirred.

The fluotantalate, dissolved in 200 c.c. boiling water, was slowly added. Solution evaporated to 150 c.c., allowed to cool overnight, then filtered. Filtrate extracted with ether and 12N.H_2SO_4 - an oil separated.

Tests.

Method as for tungstoniobic acid (p. 77).

With tannin gives a yellow precipitate, ∴ Ta present.

Hence the oil contains tungstotantalic acid.

Vanadotungstic Acid and Vanadyltungstic Acid.

Preparation.

2.5 gm. V_2O_5.

30 gm. Na_2WO_4.

The sodium tungstate was dissolved in 200 c.c. of hot water.

The V_2O_5, dissolved in NaOH solution, was added to the sodium tungstate solution, and the whole was heated, stirred and made faintly acid to litmus with H_2SO_4.

Allowed to cool overnight, then filtered and extracted with ether and 12N.H_2SO_4 - a red oil separated.

The red oil was filtered through a cotton-wool plug and evaporated to dryness to remove the ether. Residue extracted with cold water and filtered.

Filtrate reduced with SO_2 - solution turned black.

Black solution.

Extracted with ether and 12N.H_2SO_4 - a black oil separated. Oil filtered through a cotton-wool plug, then evaporated to dryness in an atmosphere of CO_2. Residue dissolved in cold water and acidified with H_2SO_4. $KMnO_4$ solution added - decolorised.

The black oil must therefore contain the vanadyl radicle (VO_2 or V_2O_4) in the form of vanadyltungstic acid.

Since the black oil was prepared from the red by reduction with SO_2, it follows that the red oil must contain vanadic acid in the form of tungstovanadic acid.

Tungstochromic Acid.

Preparation.

5 gm. sodium chromate.

25 gm. sodium tungstate.

The tungstate, dissolved in 200 c.c. of water, was added to the chromate, dissolved in 50 c.c. of water, and the mixture made faintly acid to litmus with H_2SO_4.

The solution was heated for two hours, then allowed to cool, filtered, chilled in ice, and extracted with ether and 12N.H_2SO_4.

This gave a reddish-yellow oil.

On standing, the oil rapidly darkened in colour, and finally became green. Probably the chromic acid, being a powerful oxidising agent, was reduced by the ether.

During the extraction a solid commenced to separate. This substance was of a greenish-yellow colour and was probably a solid chromyltungstic acid; cf. 10-tungstotitanic acid (p. 52).

Note.

Since no fluoride was used in this preparation, the oil which separated could not have been metatungstic acid. (See preparation of metatungstic acid, pp. 34-36).

It must therefore have been tungstochromic acid.

Tungstomolybdic Acid.

Preparation.

5 gm. sodium molybdate.

25 gm. sodium tungstate.

The sodium tungstate was dissolved in 150 c.c. of boiling water.

The sodium molybdate dissolved in 100 c.c. of water was added and the mixture made faintly acid to litmus with H_2SO_4.

Allowed to cool overnight.

Solution divided into two portions:

(1) Extracted with ether and 12N.H_2SO_4 - precipitate formed; no oil obtained.

(2) 2 gm. NaF added, then extracted with ether and 12N.H_2SO_4 - oil separated.

Test.

Oil dissolved in hot water. Solution treated with ammonium thiocyanate + stannous chloride - red coloration.

Shaken with ether: red-coloured compound dissolved in ether.

$\therefore$ Mo present.

Hence the oil contains tungstomolybdic acid.

Note.

On leaving the oil to stand it changed colour, and finally became dark green. This was probably due to reduction of the molybdic acid by the ether.

Tungstoperchloric Acid.

Preparation.

15 c.c. of perchloric acid solution (sp. gr. = 1.12)

25 gm. of sodium tungstate.

The sodium tungstate was dissolved in boiling water and the solution made just acid to litmus with H_2SO_4.

The perchloric acid solution was run in, drop by drop, with stirring. Solution allowed to cool, chilled in ice and extracted with ether and 12N.H_2SO_4 - yellow oil separated: this oil quickly darkened and became violet in colour.

Note.

Since no fluoride was used in this preparation, the oil which separated could not have been metatungstic acid (See preparation of metatungstic acid, pp. 34-36).

It must therefore have been tungstoperchloric acid.

Tungstoferric Acid.

(1) Preparation from potassium ferrifluoride.

25 gm. of sodium tungstate was dissolved in 150 c.c. of water.

The solution was made just acid to litmus with H_2SO_4, heated to boiling and stirred continuously. 5 gm. of potassium ferrifluoride was added in half-gram lots at intervals of an hour.

When all the ferrifluoride had been added, the solution was allowed to cool, filtered and extracted with ether and 12N.H_2SO_4 - this gave a dark-brown oil..... (1)

(2) Preparation from ferric chloride.

25 gm. of sodium tungstate was dissolved in 150 c.c. of boiling water and the solution made just acid to litmus.

5 gm. of ferric chloride (anhydrous), dissolved in 200 c.c. of water, was added from a dropping-funnel with a capillary jet, which delivered one drop per second.

Solution allowed to cool, filtered, and the filtrate divided into two portions:

(a) Extracted with ether and 12N.H_2SO_4 - precipitate formed, but no oil.

(b) 2 gm. NaF added, then extracted with ether and 12N.H_2SO_4 - dark-brown oil separated..... (2)

Both specimens of oil, (1) and (2), were tested as follows, and each gave the same result:

Test.

Oil dissolved in boiling water and solution made strongly alkaline with NaOH - reddish-brown precipitate.

∴ Fe present.

Hence the oil contains tungstoferric acid.

Formulation.

Before proceeding to discuss the uses of fluoride in the syntheses of heteropoly-tungstic acids, it is necessary that one should have some idea of the probable formulae of these compounds.

The well-known boro-, silico- and phospho-tungstic acids have the formulae:

$H_9\left[B(W_2O_7)_6\right] \times H_2O$ - tungstoboric acid.

$H_8\left[Si(W_2O_7)_6\right] \times H_2O$ - tungstosilicic acid.

$H_7\left[P(W_2O_7)_6\right] \times H_2O$ - tungstophosphoric acid.

Each of these acids can be expressed by the general formula

$$H_{12-n}\left[R^n(W_2O_7)_6\right]$$

where "R" is an element (phosphorus, silicon or boron) of valency "n".

It is extremely probable that the new heteropoly-tungstic acids will also conform to this type.

(Tungstotitanic acid has proved to be $H_8[Ti(W_2O_7)_6]$; see p.57).

If it be assumed that the general formula $H_{12-n}[R^n(W_2O_7)_6]$ holds good throughout the entire series, the following formulae are obtained:

Tungstoargentic acid	-	$H_{11}[Ag(W_2O_7)_6]$
Tungstozincic acid	-	$H_{10}[Zn(W_2O_7)_6]$
Tungstoferric acid	-	$H_9[Fe(W_2O_7)_6]$
Tungstotitanic acid	-	$H_8[Ti(W_2O_7)_6]$
Tungstoniobic acid	-	$H_7[Nb(W_2O_7)_6]$
Tungstomolybdic acid	-	$H_6[Mo(W_2O_7)_6]$
Tungstoperchloric acid	-	$H_5[Cl(W_2O_7)_6]$

For a clear understanding of what follows, the assumption of these formulae is essential.

The Uses of Fluoride in the Preparation of Heteropoly-Tungstic Acids.

A. - Tungstotitanic Acid.

To obtain 12-tungstotitanic acid, $H_8\left[Ti(W_2O_7)_6\right] \times H_2O$, in which the titanium forms part of the complex negative radicle, one must use a titanium compound in which the element is present, not as a titanic salt, which would yield Ti^{++++} ions, but as a titanic acid (ionised as $TiO_4^{\equiv}$).

Since no soluble oxy-titanate is known, the synthesis can only be carried out by using

(a) Freshly-precipitated titanic acid

or

(b) Potassium fluo-titanate, $K_2TiF_6.2H_2O$ (which is soluble in water).

As explained under the preparation of 12-tungstotitanic acid (see p. 44), the method involving a saturation of sodium paratungstate with titanic acid was found to be too laborious, so attention was concentrated on the potassium fluotitanate + sodium paratungstate synthesis, which was more easily controlled and more quickly carried out.

The equation suggested for this reaction is:

$$5Na_2O.12WO_3 + 2K_2TiF_6 + 2H_2O = Na_4H_4\left[Ti(W_2O_7)_6\right] + 6NaF + 4KF + TiOF_2 .$$

Hence, though fluo-titanate is used, hydrolysis to oxy-titanate takes place before the titanium enters the nucleus of the complex negative tungstotitanate ion.

Thus fluoride was used in this instance primarily because potassium fluotitanate happened to be the only water-soluble titanate available.

B. - Tungstoferric, Tungstocupric and Tungstoargentic Acids.

For the preparation of tungstoferric acid (see p. 83), a solution of ferric chloride was added slowly to a solution of sodium paratungstate and the resulting product divided into two parts:

(1) Extracted with H_2SO_4 + ether - precipitation of tungstic acid; no tungstoferric acid obtained.

(2) NaF added and solution extracted with ether and H_2SO_4 - tungstoferric acid obtained.

Here the addition of sodium fluoride meant all the difference between success and failure.

It is probable that both portions of the solution contained sodium tungstoferrate, generated thus:

$$5Na_2O.12WO_3 + 2FeCl_3 + 2H_2O = Na_5H_4\left[Fe(W_2O_7)_6\right] + 5NaCl + FeOCl.$$

Case (1).

Addition of H_2SO_4 liberated tungstoferric acid, $H_9\left[Fe(W_2O_7)_6\right]$, which, in the strongly acid solution, reacted to give ferric sulphate:

$$2H_9\left[Fe(W_2O_7)_6\right] + 3H_2SO_4 = Fe_2(SO_4)_3 + 24WO_3 + 12H_2O.$$

Thus positive ionisation of the iron resulted in complete decomposition of the tungstoferric acid, in which the iron must exist in the negative radicle.

Case (2).

Hydrofluoric acid was liberated.
In hydrofluoric acid solution, iron is not ionised as Fe^{+++}, and probably exists as a fluoferric acid.

Hence the addition of fluoride during extraction of a solution of sodium tungstoferrate is necessary, because the hydrofluoric acid liberated represses positive ionisation of the iron in tungstoferric acid, and thus prevents decomposition of the complex.

The function of the fluoride was exactly similar in the cases of tungstoargentic and tungstocupric acids.

Thus we see that, in cases where the nucleus of the heteropoly-tungstate anion is occupied by an element of basigenic character (e.g. Ag.), the free acid can only be extracted in presence of fluoride, which represses the positive ionisation of the basigenic element, and therefore prevents the decomposition of the heteropoly-acid which would otherwise take place.

C. - Tungstoniobic, Tungstotantalic and Tungstomolybdic Acids.

For the preparation of tungstoniobic acid (see p. 76) the solution of sodium niobate + sodium tungstate was divided into two parts:

(1) Extracted with ether and H_2SO_4 - niobic acid + tungstic acid precipitated; no oil obtained.

(2) NaF added then extracted with ether and H_2SO_4 - tungstoniobic acid obtained.

Case (1).

Decomposition resulted from the precipitation of niobic acid, which is insoluble in water, and in mineral acids other than hydrofluoric acid.

Case (2).

A soluble oxyfluoniobic acid - probably $2HF.NbOF_3$, i.e. $H_2\ NbOF_5$ from which the well-known potassium oxyfluoniobate, $2\ KF.NbOF_3$ is derived; cf. C. Marignac (Ann. Chim. Phys. [4] 8 [1866] 5, 49, 68) - was formed, and the niobic acid was therefore retained in solution until the tungstoniobic acid could be extracted by the ether.

Here, then, fluoride is necessary because it prevents precipitation of niobic acid.

The function of the fluoride appears to be somewhat similar in the cases of tungstotantalic and tungstomolybdic acids.

Summary.

The classical idea (based on a study of the boro-, silico- and phospho-tungstic acids) that each of the heteropoly-tungstic acids is formed by combination of tungstic acid with another acidic oxide can no longer be regarded as correct.

The heteropoly-series now includes compounds formed by combination of tungstic oxide with oxides of definitely non-acidic character; and indeed elements of every Group, from I to VII, of the Periodic Table are now to be found in the heteropoly-tungstic series.

Thus:

Group.	Element.	Heteropoly Acid.
I.	Ag	Tungstoargentic.
II.	Zn	Tungstozincic.
III	Fe*	Tungstoferric.
IV.	Ti	Tungstotitanic.
V.	Nb	Tungstoniobic.
VI.	Cr	Tungstochromic.
VII.	Cl	Tungstoperchloric.

(*Fe is usually placed in Group VIII, but it is here inserted in Group III because of its tervalency).

Time did not permit of an attempt being made to prepare a heteropoly-tungstic acid containing one of the precious metals of Group VIII; but, in view of the behaviour of 7-valent

chlorine, there seems to be no reason to doubt that tungsto-platinic or tungsto-osmic acid could be synthesised.

In fact, the probability is that, of all the elements in the Periodic Table, only the Inert Gases, the Alkali Metals, and possibly the Alkaline Earths, are exempt from heteropoly-tungstic acid formation.

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